Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

1. Experiment Sections

1.1 Reagents

DNA sequences were synthesized by Sangon Inc. (Shanghai, China), as shown following:

Probe DNA 1: 5'-AGTCAGTGTGGAAAATCTCTAGC-FAM-3'

Target DNA: 5'-GCTAGAGATTTTCCACACTGACT-3'

Single-base mismatch DNA: 5'-GCTAGAGATTGTCCACACTGACT-3'

Probe DNA 2:

5'-TCTCTCAGTCCGTGGTAGGGCAGGTTGGGGTGACT-FAM-3'

Probe DNA 1 is the complementary sequence of HIV-1 U5. FAM is fluorescein-based dye. Target DNA is HIV-1 U5 sequence. Single-base mismatched DNA has a single-base mismatch (in underline) compared with target DNA. Probe DNA 2 is the anti-thrombin aptamer.

Dithiooxamide (H_4*dtoa*) was purchased from Intenational Laboratory, USA. Thrombin was bought from Sigma (St. Louis, MO). Bovine serum albumin (BSA) and human IgG antibody were bought from Dingguo Biotech (Beijing, China). Other chemicals employed were all of analytical grade.

DNA buffer solutions were prepared by dissolving DNA into 30 nM Tris-HCl buffer (pH 7.4, containing 100 mM NaCl and 5 mM $MgCl_2$).

1.2 Preparation of Cu(H_2*dtoa*)

Cu(H_2*dtoa*) was synthesized by previous reports[1]. Briefly, 5% H_4*dtoa* ethanol solution was added to lukewarm $CuSO_4$ aqueous solution with stirring. The black precipitate was washed with water and ethanol several times, and then separated from the supernatant fraction with the centrifuge. The gelatinous precipitate was centrifugated and dried in an evacuated desiccator for the following experiment.

1.3 Characterization of Cu(H_2*dtoa*)

IR spectra were determined by a Nicolet 6700 FT-IR Spectrometer in the range 400 to 4000 cm^{-1} choosing KBr as medium. The photographs were taken with an Panasonic DMC-FX35 digital camera. IR (/cm^{-1}) of production: 3240 /cm^{-1}; 1534 /cm^{-1}; 1505 /cm^{-1}; 1195 /cm^{-1}; 1046 /cm^{-1}; 860/cm^{-1}; 781/cm^{-1}, which is similar with the previous report[1].

1.4 Preparation of complex probe DNA/ Cu(H_2*dtoa*)

0.2 mg Cu(H_2*dtoa*) synthesized in the above was dispersed in 1 mL distilled water by sonication. Next, the solution was mixed with 50 nM probe DNA with oscillation at room temperature in order to obtain a symmetrical and limpid solution. The mixture containing complex probe DNA/Cu(H_2*dtoa*) was interacted with different targets with rocking in 37 ^oC for 4 h (except for the temperature and time-course study). The obtained complex was directly used for the following test.

1.5 Fluorescent Measurements

The fluorescence measurements were performed at room temperature on a Varian Cary Eclipse Fluorescence Spectrophotometer except specific indication. The emission spectra were collected from 500 to 650 nm with the excitation wavelength of 480 nm. Both the excitation and emission slit widths were set to 10.0 nm. The fluorescence intensity at 518 nm is used for quantitative analysis.

The quenching efficiency (Q_E, %) was calculated by the formula: $Q_E = (1-F_M/F_0)\times 100\%$, where F_M and F_0 are fluorescence intensities at 518 nm in the presence and the absence of Cu(H_2*dtoa*). Fluorescence recovery was calculated by the formula: $RE=(F_T/F_M-1)\times 100\%$, where F_T and F_M are fluorescence intensities at 518 nm in the presence and the absence of target after the introduction of Cu(H_2*dtoa*).

2. Optimization of condition

The operational conditions should be optimized for better assay. Firstly, the dosage of Cu(H_2*dtoa*) should be chosen properly. Once Cu(H_2*dtoa*) is overdosed, it will adsorb the target and go against the restoration of fluorescence. As shown in Figure S1A, upon the introduction of 0.2 mg/mL Cu(H_2*dtoa*) to probe DNA (50 nM), it is found that fluorescence intensity decreases gradually until 20 μL Cu(H_2*dtoa*) is introduced. It is indicated that 20 μL Cu(H_2*dtoa*) is enough to adsorb probe DNA in the solution, and at this condition, the Q_E of Cu(H_2*dtoa*) to probe DNA is 84.6 %. Hence, 20 μL Cu(H_2*dtoa*) are used to following experiment.

The fluorescent recovery has a relationship with the incubation time of complex probe DNA/Cu(H_2*dtoa*) and target. Hence, the incubation time is investigated. The result is shown in Figure S1B. The fluorescent recovery is done with vibration in

37°C water bath. Upon increasing incubation time, more adsorbed probe DNA is released from Cu(H_2*dtoa*), resulting in the recovery of fluorescence gradually. When the incubation time was longer than 4 h, the intensity was no longer increased, showing that it reaches a balance between probe DNA/Cu(H_2*dtoa*) and probe DNA/target. Thus, 4 h is chosen as the incubation time.

Reference

1. S. Kanda, A. Suzuki, K. Ohkawa, Ind. Eng. Chem. Prod. Res. Dev. 1973, 12, 88.

Table S1 Fluorescence intensity changes to different kinds of solutions

MOF Fluorescence	$CuSO_4$	H_4dtoa	$Cu(H_2dtoa)$
Fo:(FAM-DNA)	493	490	485
F_M:(FAM-DNA+MOF)	62	460	75
Q_E	87.42%	6.12%	84.53%

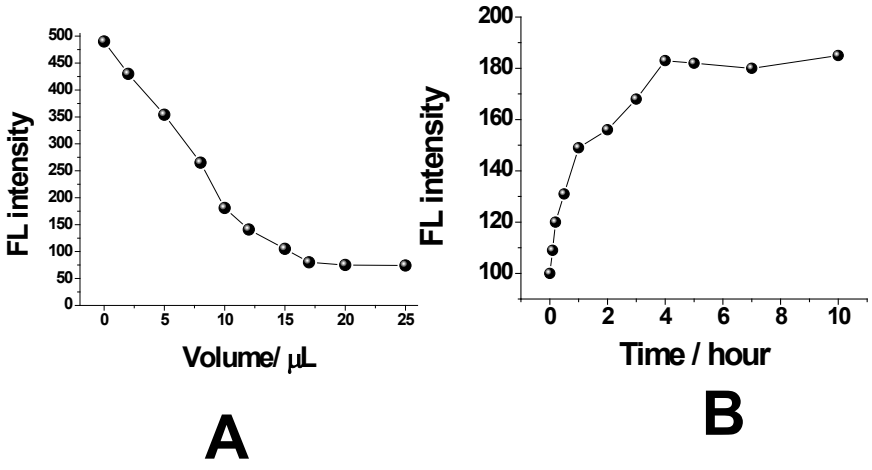

Figure S1 (A) Fluorescence intensity of probe DNA upon the introduction of Cu(H_2*dtoa*). (B) The influence of the incubation time between the complex probe DNA/ Cu(H_2*dtoa*) and target on the fluorescence intensity. The fluorescence intensity is collected at 518 nm.